

An Analysis of Air Pollution Control Technologies for Shipyard Emitted Volatile Organic Compounds (VOCS)

**U.S. DEPARTMENT OF TRANSPORTATION
MARITIME ADMINISTRATION**

in cooperation with

**National Steel and Shipbuilding Company
San Diego, California**

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE MAR 1993		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE An Analysis of Air Pollution Control Technologies for Shipyard Emitted Volatile Organic Compounds (VOCS)				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Surface Warfare Center CD Code 2230-Design Integration Tools Bldg 192, Room 128 9500 MacArthur Blvd, Bethesda, MD 20817-5700				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 48	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

**AN ANALYSIS OF
AIR POLLUTION CONTROL TECHNOLOGIES
FOR SHIPYARD EMITTED
VOLATILE ORGANIC COMPOUNDS (VOCs)**

**Prepared by
Thomas J. Snider
for
The National Shipbuilding Research Program (NSRP)
In cooperation with
NATIONAL STEEL AND SHIPBUILDING COMPANY**

March 1993

CONTENTS

	Executive Summary	i
1.0	Introduction	1
2.0	Ship Building and Repair VOC Emitting Operations	3
	The Hull • Interior Tanks and Compartments • The Superstructure Hull Construction Blocks • Component Parts • Metal Stock Priming	
3.0	Description of VOC Control Technologies	6
3.1	Incineration/Oxidation	7
	3.1.1 Incineration	7
	3.1.2 Oxidation	9
3.2	Sorption Processes	11
	3.2.1 Adsorption	11
	3.2.2 Absorption	15
3.3	Condensation	16
3.4	Hybrid Systems	17
4.0	Examples of Recent Innovative Pilot-Scale Systems and Studies	19
5.0	Application of VOC Emission Control Systems to the Shipbuilding Industry	25
5.1	Capture of the Airstream	25
	Construction Blocks • Component Parts • Pre-Construction Primer Coating	
5.2	Control of VOCs in the Airstream	29
	Destruction • Removal	
6.0	Alternatives to Control Technology	33
7.0	Conclusions	35
	Appendix	
	References	
	Acronyms	

EXECUTIVE SUMMARY

Amendments to the Clean Air Act (CAA) have prompted the need to reduce Volatile Organic Compound (VOC) emissions from industrial operations. One approach to VOC reduction is through air pollution control technology to remove the contaminants from the exhaust airstream of VOC generating processes.

Although a variety of processes in the Ship Building and Repair Industry generate VOCs, coating operations have the greatest potential for achieving large reductions in emissions. Due to the distinctive nature of the operations, practical installation and use of air pollution control equipment within shipyards is not simple. Shipyard operations are intermittent in time, conducted at a variety of constantly changing locations within the facility, and use a wide array of coatings with many different formulations. Coating operations can be divided into several groups, each of which presents a unique situation. The element common to most of these operations is a low concentration of VOCs in a large volume air.

There are three fundamental categories of VOC control technology. These are: incineration/oxidation; sorption processes; and condensation. In some applications these technologies are combined into hybrid systems.

- 1 Incineration and oxidation destroy VOCs by breaking them into smaller, less harmful molecules. Incineration does this thermally, either directly with very intense heat or at more moderate temperatures through the use of a catalyst. Oxidation breaks apart VOCs with an oxidizing substance such as ozone.

- Sorption urocesses capture and hold VOC molecules with another media. Two sorption processes are described adsorption and absorption. Adsorption accumulates VOC molecules onto a surface through electro-chemical attraction. Absorption accumulates VOC molecules through inter-penetration into other media.
- Condensation removes VOCs from an airstream by chilling them below their dew point, causing them to condense into droplets. These droplets are then collected onto a surface for removal.
- Hybrid systems use the strength of one technology to compensate for the weakness in another by combining two or more processes into one unit.

Pilot-scale studies have been conducted within paint spray booths to explore how feasible these technologies are under various conditions. Because it is difficult to remove low concentrations of VOCs from a contaminated airstream, innovative methods to increase concentrations within a booth are being tried. These methods include air recirculation and air stratification.

To apply any of these air pollution control technologies, two aspects must be addressed; capture of the air stream containing the VOCs, and control or removal of the VOCs from that captured airstream. The dilemma that exists is to capture enough of the emitted VOCs to make the process practical, maintain a high VOC concentration for acceptable control efficiency, and keep the total volume of air low to maintain economic feasibility.

Alternatives to air pollution control equipment to reduce VOC emissions exist. An increase in transfer efficiency will reduce the total volume of coatings used and thus reduce total emissions. Under investigation is the use of supercritical fluids as a replacement for part of the solvent portion of coatings. Research continues on coating reformulation to reduce the solvent content while preserving performance characteristics.

Coating reformulation could eliminate VOC emissions from coatings at all shipyards without individual investment in air pollution control equipment.

1.0 INTRODUCTION

In 1990 the federal Clean Air Act (CAA) was amended. Title III of the CAA amendments created a list of Hazardous Air Pollutants (HAPs) to be regulated. Title III established a two phased approach to reduce HAPs emissions: Phase I - development of Maximum Achievable Control Technology (MACT) standards, and, Phase II - risk-based emission reductions.

MACT standards are defined as the maximum degree of reduction in emissions taking into consideration the cost of achieving such emissions reduction, and any non-air quality health and environmental impacts and energy requirements achievable for new or existing sources. They will be based upon the best demonstrated control technology and practices established for regulated source categories. The intent is to reduce HAP emission levels to standards established by the Environmental Protection Agency (EPA). Techniques used to achieve MACT standards include air pollution control equipment industrial process changes, product reformulation product substitution production control procedures, work practice or operational standards, or any combination of these.

Provisions within the CAA to reduce Volatile Organic Compound (VOC) emissions affect the coating operations conducted by the ship building and repair industry. VOCs are identified in almost every coating system in the marine industry as the solvent component of the paint. Most of these VOCs will be listed as HAPs within the CAA amendments and will therefore require some type of control to reduce their emissions.

Title I of the Clean Air Act Amendments require the development of a Control Technique Guideline (CTG) for the Shipbuilding and Ship Repair Industry. The purpose of the CTG is to control the emissions of VOCs and particulate matter that originate

from coatings and solvents and reduce them to the level the EPA determines achievable through the Best Available Control Measures (BACM).

The NSRP SP-1 Facilities and Environmental Effects Panel and SP-3 Surface Preparation and Coating Panel both deserve recognition for their foresight in identifying the need for an evaluation of emission control technologies for VOC reduction and how these technologies apply to the Ship Building and Repair Industry. This report describes various methods to reduce VOC emissions through the use of air pollution control techniques, and evaluates the application of control devices to shipyard operations. Basic technologies are described along with specific examples and applications.

2.0 SHIPBUILDING AND REPAIR VOC EMIITING OPERATIONS

A variety of processes in a typical shipyard produce VOC emissions, including decreasing operations, small parts cleaning and paint spraying. Primarily due to volume, the process that has the potential to generate the greatest quantity of VOCs in a shipyard is paint spraying or coating operations.

Paint operations in a shipyard can be divided into several groups: the hull; interior tanks and compartments; the superstructure; hull construction blocks; component parts; and metal stock priming. Each of these groups present their own individual conditions.

The Hull

Hull painting is usually accomplished while a ship is in dry dock or on a ship building ways. Characteristics unique to the hull of a ship are the relatively flat surface and immense size. A hull ranges from 300 to over 1000 feet from bow to stern 50 to 120 feet in breadth, and 30 to 80 feet from top to bottom.

Interior Tanks and Compartments

Interior tanks and compartments generally consist of enclosed spaces with limited access. They range in size from the interior compartments of an oil tanker to small tanks used for ballast compensation.

The Superstructure

The superstructure of a ship consists of the exposed decks, deck houses, and structures above the deck such as antennas or radar arrays. These structures are characterized by a wide range of shapes and sizes. Structures such as deck houses have flat surfaces with tight comers and angles; antennas, radar arrays and other structures are curved cylindrical long and linear, or any combination.

Hull Construction Blocks

Hull construction blocks, comparable to children's building blocks, are common in modern ship construction technique. Painting or coating a block occurs before it is attached to the main body of the ship. Blocks range in dimension from 10 to 60 feet in length, breadth and width. Any combination of dimensions may exist depending upon the design of the ship; one block may measure 40 by 25 by 20 feet another 60 by 40 by 10 feet. Grand blocks, usually made by attaching together two or more construction blocks, are even larger. The current trend for increasing ship construction efficiency is toward this grand block concept. Construction blocks are characterized by large fiat surfaces, many facets and angles, and a great range in size and shape.

Component Parts

Component parts are flat, curved, or convoluted. Parts such as pipes and ducts are linear if in individual sections or complex if manifolded together. Anchor chains are difficult to affectively manipulate, especially if within a confined space. In ship repair work many component parts are removed from the ship prior to painting. Component parts for new ship construction can be painted before installation.

Metal Stock Priming

Prime coating of raw metal stock is perhaps the most routine in nature of the coating process found in a shipyard, although not all shipyards use primer coating. Metal stock consists of flat sheets or linear angles, each with consistent shape and size. The metal is coated with a pre-construction primer to prevent oxidation and rusting of the stock during construction operations. The operation is usually conducted at one localized area of a shipyard in an automated or semi-automated facility. Because it is a temporary protective coating, the pre-construction primer used is chosen by the shipyard and does not change in composition with each ship under repair or construction.

Coating operations in a shipyard are not continuous repetitious operations such as found in a production paint line in an automobile assembly plant. Coating requirements in the Ship Building and Repair Industry differ with each ship. Coating requirements for Navy vessels differ from those required by commercial clients. The geographic area where the ship is intended to operate dictates the performance requirements of a coating. Therefore coatings used vary from ship to ship in both the composition of solids and in the organic solvent portion responsible for VOC emissions.

3.0 DESCRIPTION OF VOC CONTROL TECHNOLOGIES

VOC control technologies can be divided into three fundamental categories: Incineration/Oxidation, Adsorption/Absorption, and Condensation. Each technology has inherent advantages and disadvantages depending upon its application. Hybrid systems, or combinations of these technologies, are attempts to overcome the weakness of one technology with the strength of another.

These technologies are applied to VOC emitting operations typically through add-on control devices attached downstream of the air flow. The devices are usually permanent installations that do not lend themselves to portability.

The efficiency of a control device is a function not only of its ability to remove or “control” the VOCs within a volume of air, but also the ability of the device to “capture” the airstream which contains the VOCs. The total efficiency of a control device on a process is the ratio of the VOCs removed from the air stream that passes through the device, versus the total amount of VOCs that are generated by the process. This takes into account the VOCs contained within air that never reaches the control device, and VOCs that are emitted from any of the coated parts after they have passed through the coating process.

The individual solvents within a coating have an affect on the ability of these control techniques to remove the VOCs from the waste airstream. Characteristics of the VOCs such as vapor pressure, BTU value, molecular size and weight, individual ionic properties, hydrophilic or hydrophobic properties, and Lower Explosion Limits (LEL), will either improve or retard a devices control efficiency.

The following section describes the major technological methods used to remove VOCs from a contaminated airstream and provides a description of hybrid systems.

3.1 INCINERATION/OXIDATION

VOCs can be broken into the simpler molecules of carbon dioxide and water by incineration or oxidation. Incineration accomplishes this breakup by thermal means; oxidation requires the use of an oxidizing substance such as ozone to break the VOCs apart. Although these are not technical definitions, they are useful to describe the basic principles.

3.1.1 Incineration

Incinerators can be separated into two types: thermal and catalytic. For incineration the factors to keep in mind are the three T's; Time, Temperature and Turbulence. The contaminated airstream must be maintained at a high enough temperature for a sufficient length of time to destroy the VOCs, with adequate mixing to assure all parts of the airstream are affected.

Thermal incineration (or direct flame) is conducted at essentially atmospheric pressure and within a temperature range of 850° to 1,800° Fahrenheit (1,400° F is typical). Residence time within the combustion chamber is typically between 0.3 to 1.0 seconds with an airstream velocity between 15 and 25 ft/sec. When a contaminated airstream has a low BTU value, a supplemental fuel is needed to support combustion. Typical fuels used are natural gas or fuel oil. Supplemental fuel are also used to balance fluctuations in the VOC concentration of an airstream. The extra fuel moderates the BTU loading to the incinerator to keep the process at a steady state.

To reduce total energy requirements many incineration systems recover the generated heat. Primary heat recovery uses hot gases from the incinerator combustion chamber to preheat the incoming VOC contaminated air. The expected heat recovery efficiency is approximately 35 percent. The equipment frequently used is a tube and shell heat exchanger. A limiting factor in heat exchanger design is the dew point of materials within the hot flue exhaust gas. If the flue gas is cooled below the dew point of its constituents, acids may form. These acids can damage the heat recovery system and any other downstream appurtenant structures. This is especially characteristic of an airstream containing halogenated compounds. The use of corrosion resistant materials of construction, such as stainless steel, is expensive. A more practical solution may be to avoid excessive cooling of the flue gas, limiting the heat exchange ability.

Secondary heat recovery involves the use of hot incinerator exhaust as supplemental heat for other processes at a facility, such as ovens, tanks, or space heating. The secondary process should be located in close proximity to the incineration process. Due to these potential applications, secondary heat recovery is more appropriate for continuous incineration processes.

Catalytic incineration can take place at temperatures lower than that required for thermal incineration. Catalytic incineration has an approximate temperature range of 500° to 900° Fahrenheit. The catalyst promotes combustion at lower temperatures by decreasing the activation energy required for chemical reaction. Typical catalysts include assorted noble metals such as platinum palladium, ruthenium or rhodium. These catalytic metals are usually deposited onto a supporting structure of honeycombed or pelletized alumina. The lower combustion temperature of catalytic incinerators result in lower supplemental fuel consumption rates than direct flame thermal incinerators.

3.1.2 Oxidation

VOCs can also be destroyed through the use of oxidizers. Oxidizers break the organic molecules and combine with the parts. The most common oxidizer used is ozone, or O_3 . Ozone is highly reactive and very efficient at oxidizing VOC molecules. This process is often combined with a photolytic reaction. A photolytic reactor utilizes a tuned ultraviolet light frequency to enhance the ozone oxidation process.

Ozone can be purchased and stored in bulk or generated on-site. Due to ozone's highly reactive nature, generation on-site at the rate required for the intended oxidation process is generally the less hazardous practice. One process of generating ozone is similar to that of the photolytic reactor described above. On-site generators produce the ozone photochemically by passing filtered ambient air through reaction chambers. Here the air is irradiated by ultraviolet light and a portion of the oxygen in the air dissociates and recombines to form ozone (O_3) and other reactive oxygen based compounds. These generated reactive compounds are then used in the VOC destruction process.

Incineration technology is well established and presents no significant engineering problems of its own. If the system is carefully designed, the process can achieve high VOC destruction efficiency and can be effective over a wide range of VOC compositions. With the use of supplemental fuel, fluctuations in the VOC concentration within the airstream is not a limiting factor. The installed systems are easy to operate and require comparably minor maintenance. Small volumes of solid or liquid waste are produced; ash and soot and perhaps acidic waste depending upon the mixture of VOCs in the process airstream.

Incineration technology has some disadvantages. The capital cost for system installation is generally high. If the VOC content of the airstream to be controlled is low, the cost

of supplemental fuels will add to the operating costs. The availability of supplemental fuels in sufficient volume must also be considered.

Incineration also produces a number of secondary pollutants. Nitrogen oxides, resulting from thermal fixation of nitrogen in the ambient air, are produced. Carbon monoxide, ketones, aldehydes, and organic acids that are a result of incomplete combustion of organic materials may also be emitted. Incineration of halogenated compounds may produce acids, such as hydrochloric or hydrofluoric, that attack the metal in the exhaust system. These secondary pollutants may require their own separate air pollution control device and special construction materials. These requirements add to the cost of the entire system.

Catalytic systems may lower the supplemental fuel requirement of a incineration system, but catalysts present other problems. Catalyst are eventually consumed in the system and must be periodically replaced. Additionally, catalyst are easily fouled in the system. Materials such as arsenic, mercury, phosphorus, sulfur and halogens can poison catalytic metals. Solid or liquid particles can cover or coat them. Replacement is expensive. The typical effective life-span of catalytic metals, if conditions are favorable, is three to five years.

Because oxidation systems do not require supplemental fuels, they have a potential advantage over straight incineration systems. Oxidation systems are also likely to produce less secondary pollutants. However, these systems offer slightly lower destruction efficiencies, the technology is not as well established when compared to incineration systems, and there is less information available on their reliability. In addition because ozone is an extremely aggressive oxidizer, it presents a hazard and a concern for safety.

3.2 SORPTION PROCESSES

Sorption processes take up VOC molecules and hold them within another media. Two sorption processes are described; adsorption and absorption.

3.2.1 Adsorption

Adsorption is a process where by molecules of one substance accumulate on the surface of another. The process can occur between any two physical phases of materials that have a separate interface, for example, gas-liquid gas-solid liquid-solid, or liquid-liquid. The material accumulating or being concentrated is termed the adsorbate; the material acting as the adsorbing surface or interface is called the adsorbent. In context to this report the adsorbate originates from a gaseous phase. Three types of adsorption mechanics can be distinguished:

- 1) electrical attraction of the adsorbate to the adsorbent;
- 2) van der Waals attraction; and,
- 3) chemical attraction.

Adsorption of the first type, electrical attraction, is also called “exchange” adsorption. This is a process in which the ions of one material concentrate as a result of electrostatic attraction to charged sites on the other surface. Adsorption resulting from van der Waals forces, named after the scientist who first described them is sometimes called “physical” or “ideal” adsorption. Van der Waals forces are attractive forces that exist between any two particles or substances and can be thought analogous to the force of gravity. In this case, the adsorbed molecules are not fixed to a specific site on the adsorbent surface, but are free to move along the interface. The third type of adsorption involves a chemical reaction between the adsorbate and adsorbent. This is also called “chemisorption”. Chemisorption exhibits high energies of adsorption; the adsorbate forms strong localized bonds at chemically active sites on the adsorbent. The molecules are not considered free

to move on the surface or interface, and require more energy to desorb when compared to the other types of adsorption. Most adsorption processes involve a combination of these three forms.

The amount of adsorbate, or in this case VOCs, that can be removed from an airstream is a function of and proportional to the surface area of the adsorbent. An ideal adsorbent has a very high surface area, or interface, per unit volume of material. Physical factors within the adsorption device affect adsorption efficiency. These factors include temperature, pressure and humidity. In a static system, at any given temperature and pressure, equilibrium exists between the gas phase of the VOCs and the adsorbed phase. This is called the adsorption isotherm. Raising the temperature will decrease the capacity of the adsorbent; raising the pressure will increase it. Humidity can also affect the process by causing moisture to precipitate onto the adsorbent surface, displacing the target VOCs.

Physical characteristics of the VOCs affect their ability to adsorb. The driving force for adsorption is the partial pressure the VOCs have within the airstream. This partial pressure follows Dalton's Law and can be described as the pressure the VOCs would exert if they were the only vapor molecules within the airstream. The higher the vapor pressure, the greater the driving force and the greater the saturation ability and capacity of the adsorbent. Differences in the VOC mixture may cause a selective preference of the adsorbent for one VOC over another. VOC compounds with high molecular weight will adsorb differently than those with lower. Long chain molecules will adsorb differently than short chained or multi-branched. Non-polar molecules may adsorb differently than polar molecules.

The affects these differences have depend also upon the adsorbent used in the process. Activated carbon is the most commonly used adsorbent. This is due to its large internal surface area, low polarity, relatively low cost, and its ability to be

easily desorbed or regenerated. “Activated” carbon is produced by subjecting carbon to high temperature steam air or carbon dioxide, causing the carbon to fracture and produce millions of internal micropores. A typical commercially available activated carbon has a granule size of 2 millimeters and a surface area of 1000 square meters per gram of material. The variables under which the carbon is “activated and the original source of the carbon material affect the physical abilities and characteristics of the activated carbon. Because of this, care should be taken to match an activated carbon to a particular application.

As expected, carbon has a finite carrying capacity for VOCs. Once the carbon is saturated the VOCs must be removed and either collected or destroyed. This removal process is called resorption. The VOCs are desorbed by reducing the ability of the carbon to hold them. This is accomplished with high pressure steam, high temperature nitrogen gas, hot air, or by subjecting the carbon to a vacuum. High pressure steam is used for most applications. Once the VOCs are removed, the carbon has become “regenerated and is again able to adsorb VOCs. The removed VOCs can then be disposed.

New unused activated carbon has a greater adsorption capacity than carbon that has been through regeneration. This is due to the inability of the regeneration process to completely remove all the VOC molecules from within the micropore spaces. This establishes what is known as the heel; VOCs that cannot be removed by regeneration and remain within the carbon. The heel remains until the carbon is again “activated. Carbon may become fouled over time from blow through of paint solids, or may physically breakdown after a number of regeneration cycles. The carbon must again be re-activated to establish its full adsorption capacity.

A typical carbon adsorption VOC control unit consists of a tank or chamber to contain the bed of activated carbon and a mechanism to blow the contaminated airstream through it. At least two tanks of carbon are used in most applications

so that one bed can be in the active adsorption mode while the other is in the desorption process being regenerated. More tanks can be used in a system depending upon the volume of air handled the time it takes to saturate the bed of carbon and the time it takes to desorb. Carbon adsorption systems typically operate at a temperature of 80° to 110° Fahrenheit and have an air velocity of 40 to 70 feet per minute. The residence time within the carbon can be adjusted by varying the air velocity or the depth of the carbon bed. The adsorption capacity of activated carbon is highly variable and depends upon the characteristics of the carbon and the specific mix of VOCs to be absorbed. A range of 2 to 20 pounds of VOC adsorbed per 100 pounds of carbon is typical.

With an optimal blend of VOCs within the airstream and a sufficiently high concentration, adsorption systems can achieve very high control efficiencies. Advantages when compared against incineration systems include lower fuel cost and little or no generation of secondary pollutants. Because of this, regulatory permitting of an adsorption system is likely to be less complicated than with other air pollution control systems. One of the greatest advantages of an adsorption process is the ability to recover and reuse the VOC solvents. This is most effective when the solvent mix within the contaminated airstream remains unchanged over time. With this situation it may be possible to use the recovered solvent again within the original VOC generating process or in other production processes. An example is the reuse of solvents to clean equipment used in the coating operation.

Adsorption has negative features as well. The adsorption media can become fouled and ineffective, often without the knowledge of the operator. Humidity may alter the efficiency of the adsorption media and can generate organic acids that effect the system. Fluctuations in the blend of VOCs or low concentrations within the contaminated airstream can significantly lower the control efficiency of a system. With carbon adsorption, ketones in the airstream present a fire hazard

due to their high heat of adsorption. If this heat is not dissipated, the bed of carbon can ignite and burn much like charcoal briquettes in a barbecue.

3.2.2 Absorption

Absorption is considered a more mechanical process when compared to adsorption. Absorption is a process in which the molecules of one physical phase inter-penetrate uniformly among the molecules of the absorbent comparable to a sponge blotting water. In the case of gas absorption the contaminated air stream is usually brought in contact with and dissolved within an absorbing liquid. The mass transfer rate at which this absorption takes place depends upon:

- the affinity of the liquid for the VOCs;
- the concentration of the VOCs in the air stream;
- the surface area of the liquid exposed;
- the volume of VOCs already absorbed by the liquid;
- temperature; and,
- pressure.

The liquid chosen for use as an absorbent depends upon the properties of the VOCs to be controlled. Water can be used as the absorbent for water soluble VOCs such as acetone or alcohols. High-boiling point oil and other proprietary organic liquids have been used in other applications.

A typical absorption control unit consists of a raised column or tower that is packed with reticulated spheres or layered distribution trays. The packing is used to evenly distribute the liquid and increase its surface area. The liquid falls by gravity through the tower while the contaminated airstream is blown counter-currently upwards through it. The intent is to maximize the contact surface of the absorbing liquid without creating too great of an air pressure drop.

An absorption system avoids some of the problems associated with carbon adsorption such as that presented by ketones or high humidity. It is easy to increase the contacting surface of the absorbing media by adding to the height of the tower. A disadvantage of absorption systems is the difficulty of finding a practical absorbing liquid for the VOCs. This is especially difficult if the mix of VOCs fluctuates over time. Absorption is also likely to have low control efficiency for an air stream with low VOC concentrations.

A problem that exists with both adsorption and absorption processes is the need to remove the captured VOCs from the media in which they are collected so the VOCs can subsequently be disposed of or recycled. In the case of carbon adsorption this most often entails removing VOCs from steam condensate. For absorption systems it requires removing the VOCs from the absorbing liquid.

3.3 CONDENSATION

Condensation involves removing VOCs from an air stream by reducing the temperature. As the temperature of an airstream decreases, it loses its ability to hold the VOCs. The point at which the VOCs begin to condense is called the dew point. This is the same process that causes moisture in the air to condense into clouds as the temperature drops. Increasing the air pressure has a similar affect. The two factors of temperature and pressure can be used in conjunction. The temperature at which the dew point is reached can be raised by increasing the pressure of the system.

Each volatile compound has its own separate dew point temperature. Because the dew point is dependent upon the partial pressure the material exerts, the amount of compound that can be condensed at a given temperature and pressure decreases proportionately as its concentration decreases.

Two types of condensers are used in application surface condensers and direct-contact. Surface condensers operate by cooling the airstream to be controlled and providing a cold surface upon which the VOCs can condense, analogous to what occurs in an old refrigerator. Condensed VOCs can then be collected from the surface and drained into a storage tank. Direct contact condensers spray a coolant directly into the air stream to condense the VOCs and mix with the coolant. The coolant-VOC mixture is then collected.

The selection of a coolant for use in a system is dependent upon the temperature required for condensation of the VOCs. Generally the temperature of the coolant used in a system should be 10 to 15 degrees Fahrenheit below the condensation temperature of the target volatile. Chilled water can be used for condensation temperatures down to 45°; brine solutions can be used down to -30°. For lower temperatures, a chlorofluorocarbon (CFC), such as Freon, has been used. The use of CFCs as a refrigerant in these processes may change as they are phased-out in the U.S. and other countries. Replacements for CFCs will likely be identified in time.

Condensation systems can be designed to recover VOCs for re-use, however they are very energy intensive and expensive for any system that must control a large volume of air. They are also not practical for systems with dilute VOC concentrations.

3.4 HYBRID SYSTEMS

Hybrid systems combine two or more technologies into one linear process in an attempt to use the strengths of one technology to compensate for the deficiencies of another. A typical arrangement would use one process to increase the VOC concentration in the airstream prior to passing it through the next process for capture or destruction.

Hybrid systems may be useful for specific applications. An example system consists of

a carbon adsorption unit coupled to an incinerator. The carbon unit captures the VOCs from the contaminated air stream. The exhaust stream from the carbon unit in desorption mode then passes through the incinerator for destruction. In this example the advantage of the hybrid system is the effective collection and economic destruction of VOCs within the total unit process. Another hybrid system example is the combination of an ozone oxidation system with Carbon adsorption. The ozone oxidation system is used as the primary VOC removal process. Those VOCs not removed within this first process are sent through the carbon adsorption unit for secondary treatment. A portion of the ozone from the ozone generator can be used to regenerate the carbon beds.

Hybrid systems are most applicable to small scale operations. Because they combine different technologies, they are more complex and generally cost more than equally sized non-hybrid systems. In addition the efficiency of the hybrid system is reduced with each subsequent process step, or is dependant upon the one process with the lowest efficiency. Because of this, they tend to be inefficient when applied to an airstream with low VOC concentrations.

4.0 EXAMPLES OF RECENT INNOVATIVE PILOT-SCALE SYSTEMS AND STUDIES

A number of recent studies have explored new techniques to control VOC emissions. Some of these techniques use existing concepts in original ways. A description of these test and pilot-scale systems provides further insight to recent developments and research in VOC control methods.

Under sponsorship from the Environmental Protection Agency (EPA) and the United States Air Force (USAF), Acurex Corporation conducted a study of innovative VOC and Hazardous Air Pollutant (HAP) control technologies. Two control methods were chosen for pilot-scale evaluation: Fluidized-Bed Catalytic Incineration (FBCI) and Carbon Paper Adsorption Catalytic Incineration (CPACI). The pilot-scale test site was a paint spray booth at McClellan Air Force Base. A portion of the exhaust from the spray booth was drawn off to conduct the tests. The VOC concentration of the air stream ranged from 30 to 752 parts per million (ppm), with an average of 132 ppm. Particulate and VOC emissions were evaluated in the tests.

The FBCI pilot system was sized to handle an air flow of approximately 500 CFM. The VOC contaminated airstream was first preheated by indirect contact with a natural gas burner. This first stage destroyed 20 to 50 percent of the VOCs. The heated air was then forced into a chamber containing a bed of fluidized catalyst-coated spheres. The bed was kept “fluidized” by the turbulence of the air blown through it. The VOCs remaining in the airstream were oxidized within this chamber. Exhaust from the FBCI system was then analyzed for VOCs. Samples were gathered in charcoal collection tubes for analysis by NIOSH Method 1300. Detection limits for the NIOSH test were 0.65 parts per billion (ppb) for one test and 1.7 ppb for another. All test results except one

indicated non-detectable levels. The one test exception detected toluene at a concentration of 2.0 ppb. Continuous monitoring of the FBCI exhaust for Carbon Monoxide (CO) and Nitrogen Oxides (NO_x) showed average levels of 59 ppm for CO and 11.6 ppm for NO_x both below the current RCRA regulatory specifications for incinerators. The results of the FBCI pilot test indicate VOC average destruction and removal efficiencies (DREs) greater than 99 percent.

The CPACI pilot test in the Acurex study was conducted at the same Air Force spray booth. The CPACI method is a hybrid system that utilizes carbon adsorption to clean the contaminated airstream and catalytic incineration to destroy the collected VOCs. During testing, contaminated air from the spray booth was passed through a cylindrically shaped, honeycombed carbon paper filter. The carbon paper cylinder continuously rotated and the contaminated air passed through approximately 7/8 of the available cylinder volume. The VOCs were collected within the carbon paper and the cleansed air passed out of the system. The remaining 1/8 of the cylinder was used for resorption of the VOCs from the carbon. Hot air passed counter-currently through this section of the cylinder at approximately 1/15 of the flow rate of the contaminated air stream desorbing and concentrating the VOCs into a smaller air volume. The desorbed VOCs were then carried to a ceramic bed catalytic incinerator for destruction.

Exhaust gas from the CPACI unit was sampled at two points; the main exhaust from the carbon paper adsorber, and the exhaust from the catalytic incinerator. Samples were analyzed for VOCs using NIOSH Method 1300. Measurable VOCs were found in only 2 out of 23 NIOSH tests performed on the carbon paper adsorber exhaust. Tests of the exhaust from the incinerator indicated measurable VOCs in 16 of the 23 tests performed. Using EPA method 25A to continuously measure total unburned hydrocarbons (TUHC) from the adsorber exhaust indicated that levels were below the detection limit. TUHC measurements made on the exhaust from the incinerator destroying the concentrated VOCs indicated a range of 1.9 ppm to 53 ppm. Ten percent of the measurements were below 10 ppm; one measurement was below the detection limit. Destruction and removal

efficiencies for the carbon paper adsorber were calculated to be greater than 99 percent for all tests except one with a removal efficiency of 98.5 percent. For the pilot test unit as a whole DREs were calculated to be greater than 99 percent for 13 out of 19 tests, greater than 98 percent in five of the tests, and 96.9 percent in one test.

Cost information from the manufacturer of the equipment indicates that for a full scale system there is a linear relationship between the desired airstream flow-rate and the capital and installation cost. This information was presented in the form of an equation. For the Fluidized Bed Catalytic Incineration system the equation is:

$$T = 37.15 \times Q^{0.944}$$

Where:

T = Total cost (\$)

Q = Flow-rate into unit (CFM)

For the Carbon Paper Adsorber catalytic Incineration system the equation is:

$$T = 6.9 \times 10^8 + 14.7 Q$$

These equations were stated to be accurate to within +/- 30 percent, thus providing only a rough order magnitude cost estimate.

Another application under study is a version of incineration using an electrically heated packed bed. This is under development by a company called In-Process Technology. VOC laden air enters the unit and flows through a stationary bed of inert material that is electrically heated to a temperature of 1800° to 2000° Fahrenheit. The VOCs react with oxygen in the bed and are oxidized. The bed material also aids in the mixing of the gases and provides a surface to facilitate oxidation. The absence of an open flame is said by the manufacturer to inhibit the formation of nitrogen oxides (NO_x). The IPT model

FP-100 used in the tests had a maximum flow rate of 100 CFM and a power consumption of 50kVA. Destruction efficiencies were found to be greater than 99.99 percent for a wide range of hydrocarbon and chlorinated solvents. Information regarding the inlet concentrations was not identified.

Reducing the volume of air reduces the total energy required to remove VOCs from an airstream. Methods to reduce the volume of treated spray booth air include: recirculation of the exhaust air; and, utilization of the natural stratification of the air within the booth.

These two methods were investigated in another collaboration of the Air Force, EPA and Acurex Corporation. Some of the major issues explored in the study were safety and health. Recirculated air has potential toxic effects on spray booth operators and painters, and additional safety concerns if the lower explosion limit (LEL) of the VOCs is reached.

For the recirculation study, a small portion of the booth air was vented through a bleed-off duct into a VOC control device to remove the contaminants. Fresh make-up air was mixed with the remaining booth air prior to recirculating back through the booth. In this way, the concentration of VOCs within the booth could be adjusted. A VOC concentration monitor was placed within the air distribution plenum. The monitor was connected to an automatic damper control for the intake and exhaust ducts. If concentrations became dangerously high, the dampers could be opened to increase the influx of fresh outside air and reduce the amount of booth air recirculated, thus diluting the VOCs.

The size of the control device needed for a recirculating booth depends upon the volume of bleed-off air. This volume depends upon the size of the booth, the rate of paint usage, the flow-rate within the booth, the duration of a typical painting cycle, and the solvent concentration desired within the booth.

The equation used to determine the mass of solvent VOCs in the booth is:

$$M(t) = \text{MP} \frac{V - m}{V_{out}} \left[1 - e^{-\left(\frac{V_{out}}{V_{booth}} t \right)} \right]$$

Where:

$M(t)$	=	The total mass of solvent in the booth at time t
“Mp	=	Rate at which solvent is released into the booth
V_{booth}	=	Booth Volume
V_{out}	=	Bleed-off volume flow-rate
t	=	Time
e	=	natural log base = 2.7182818...

OSHA in the past prohibited the use of recirculation in manned spray booths due to safety and health concerns. In December 1989 OSHA ruled that recirculation may be used. The study concluded that recirculating air back into a spray booth does not necessarily create a more hazardous working environment for the painter.

Another aspect of the study was to investigate the characteristics of air flow within spray booths. The objectives were to determine the path of pollutants (both VOCs and particulates) through the booth, and locate the areas of highest pollutant concentration. The results of the tests show that VOCs tend to stratify, or remain in separate horizontal layers, as they flow through the booth from the point of generation. Because of this, VOCs emitted at low levels in a booth may increase in concentration at that level and remain decreased in the upper levels. This indicates that partitioning a booth into two discharge flows could be a method used to reduce the volume of VOC laden air that requires pollution control. The upper discharge may be clean enough to directly exhaust to the atmosphere. The lower more VOC laden air layer can be directed to a down-sized control device. The volume of air that must be controlled will depend upon the depth

of the zone of high VOC concentration.

The study also calculated the effects of combining a stratified-flow with recirculation in a spray booth. In a combined system the VOC emission reduction is estimated to be greater than 90 percent. The bleed-off flow-rate would be lower than if stratified flow or recirculation were used separately. The results also indicate that VOC concentrations within the booth would be 30 percent less than the maximum level allowed by OSHA

5.0 APPLICATION OF VOC EMISSION CONTROL SYSTEMS TO THE SHIPBUILDING INDUSTRY

Examples of installed VOC emission control systems for shipyard coating operations do not currently exist. As discussed within the Ship Building and Repair VOC Emitting Operations section of this report (Section 3), the greatest volume of VOCs emitted by a shipyard result from coating operations. In general shipyard coating operations are intermittent in time, conducted at a variety of constantly changing locations, and use a wide array of paints or coatings with many different formulations.

The process of controlling VOC emissions in any Ship Building Industry application can be divided into two sequential procedures: capture of the air stream containing the VOCs, then consequent control or removal of those VOCs from within the captured air stream. The ability and efficiency of a VOC control device to limit emissions is dependant upon these two factors.

5.1 CAPTURE OF THE AIRSTREAM

Shipyard coating operations vary widely in character. Most of the operations are not confined to one specific location where the emissions can be easily captured. The operations that can be conducted repeatedly at one location are the spray painting of hull construction blocks and component parts, and pre-construction primer coating of metal stock. The range in size and shape of the parts to be coated and the role they have in the production process must be considered for each of these operations.

Construction Blocks

Construction blocks vary greatly in size, but are typically no smaller than a 20 foot cube. A booth used for spray painting construction blocks must be sized to accommodate the largest block. Large blocks can measure as much as 65 feet by 40 feet and even larger if “grand” blocks are considered. If more than one block at a time requires painting (not unlikely in the process of ship construction), more than a single booth is required. A booth must also be able to accommodate the placement and removal of blocks.

In a large paint booth using airless paint spray equipment the California Health and Safety Code requires a linear airflow of 60 feet per minute past the paint spray operator. The required airflow velocity is even higher if conventional paint spray equipment is used. Spray booth total airflow is estimated by multiplying the square feet of the spray booth face by the average velocity of the air. A booth large enough to handle the size range of normal construction blocks would require an air face measuring approximately 75 by 45 feet or 3,375 square feet. Assuming an air velocity of 60 linear feet per minute, a single spray booth used for painting construction blocks could have a total airflow over 200,000 cubic feet per minute (CFM).

There are a number of ways to reduce airflow volume. One method consists of movable ducts situated adjacent only to the surfaces being painted. However, with the irregular surfaces and shapes typical in construction blocks, this method would slow the painting operation and significantly hinder the construction process. Another method of reducing the airflow through a booth is to reduce the air velocity. This will increase the VOC concentration within the booth, leading to health and safety concerns for the booth operator.

Component Parts

Due to their unique sizes and shapes, component parts present a situation different from construction blocks. Some component parts are small and easily accommodated within a booth. Coating an anchor chain within a booth presents the problem of handling or manipulating the chain within an enclosure. Pipe and duct assemblies present a range of shapes, sizes and configuration. A booth large enough to accommodate this range could require a face measurement of 15 by 30 feet. Using the same method as described earlier to calculate approximate airflow, a booth this size would have a total air flow of approximately 27,000 CFM.

Pre-construction Primer Coating

Pre-construction priming of metal stock is a shipyard operation that lends itself to an enclosed booth operation. As there is regularity in the size and shape of the raw stock, the coating operation can be totally enclosed and handled automatically by an operator outside of the booth. The flow of air through the booth can be minimized, resulting in greater saturation of VOCs within the air and greater ease in capturing them.

Capture of the airstream is not feasible for most other coating operations at a shipyard because the operations must be conducted either on the outside or inside of each ship. The size of the ship prohibits conducting the coating operations within a booth. This is especially true for a repair or maintenance operation where large sections of the ship cannot be relocated. The coating operations include hull painting, coating interior tanks and compartments, and painting the superstructure of the ship. The site locations include ship building ways, graving docks, floating dry docks, berths or piers.

Air contaminated with VOCs from these coating operations could conceivably be collected by hood or cowl and conveyed through ducts to a centralized air pollution control unit. However, there are major logistical and engineering problems encountered with ducting contaminated air across a shipyard. A complex of ducts distributed throughout the shipyard would be required to reach the many separate operations conducted at any time. Collection hoods would have to be large, freely movable, and able to adapt to multi-curved and angled surfaces. The ability of a hood to efficiently collect emitted VOCs on the open-air surface of a hull or superstructure of a ship would be poor. Excess air would be entrained within the collection system further diluting the VOC concentration increasing the volume of air that must be transported and treated, and increasing the required size of the control unit. Contaminated air would be lost during the transport, decreasing the collection efficiency of the system. A centralized air pollution control device for such operations would have to handle a large range in the volume of air to be handled and the concentration of VOCs within that volume. In addition a considerable amount of power would be required to push or pull this much air to a centralized device.

As discussed in the previous section on pilot-scale systems and studies, air recirculation can be used to increase the VOC concentration in an airstream that is otherwise too dilute for efficient VOC removal. Recirculation can also be used to maintain a steady VOC concentration by varying the amount of air recirculated, thereby improving control system efficiency. But problems exist with recirculation systems. In some situations recirculation of spray booth air may be prohibited due to safety and health concerns. Product quality may also be compromised. The exhaust air from the booth contains fine particles of paint overspray as well as evaporated paint solvents. These can adversely affect the performance of the coating on the parts. Filtering of the recirculated air can remove most of the paint particles, but not the solvents. Using air recirculation may increase system costs, but increases may be offset by reductions in cost for down-sized air pollution control equipment.

Volatile organic compounds escaping from an active coating operation are not the only VOCs that must be addressed. Solvents continue to evaporate from coatings until curing is complete. As the overall efficiency of an air pollution control device is subject to the ability to first capture the emissions, VOCs emitted from parts during cure time should also be captured and controlled. This requires sheltering the coated parts and collecting VOC emissions until the coating has sufficiently cured. Because these parts can cure in a non-occupied area the flow of air can be reduced, with a resulting increase in the concentration of VOCs. However, the VOC concentration cannot be increased to such a degree that the air is too saturated for the coating to cure. The size of the area required for this is dependant upon: the size and number of parts; the rate at which the parts are coated; the type of coating and the length of the curing process; and the ambient environmental conditions such as temperature, humidity, and VOC concentration. These factors affect both the volume of air that must be captured and the concentration of VOCs within it.

5.2 CONTROL OF VOCs IN THE AIRSTREAM

Once a contaminated air stream is captured, the VOCs within it must be controlled by either destruction or removal.

Destruction

Removing VOCs from an airstream at low concentrations is difficult, especially when large volumes of air are involved. To incinerate low concentrations of VOCs in an airstream requires raising the heat of the entire volume of air to the oxidation temperature of the VOCs. The oxidation of the VOCs themselves would impart negligible heat to the reaction. A tremendous quantity of supplemental fuel is required to heat large volumes of air to sufficient oxidation temperatures. This supplemental fuel adds substantially to the operating cost of

an incineration system and increases the total air emissions of the facility. If natural gas is the supplemental fuel, limits may exist on the quantity available or the ability to deliver the volume required.

A heat exchanger or heat storage systems can improve the energy efficiency of incineration systems and reduce the amount of supplemental fuel needed. However, heat storage systems such as ceramic beds require start-up and preliminary heating time before they are effective. A heat exchanger also has a lag time before it is effective. Because of this, these methods are more applicable to continuous operations and not the batch-type processes characteristic of shipyards.

Due to the quantity of oxidizer required for VOC destruction in large air volumes, oxidation would not be a practical method for most shipyard VOC control efforts. Many of the same problems identified with supplemental fuels are encountered with oxidation systems; difficulty in supplying a sufficient amount of oxidizing material and high cost to operate.

Removal

Low VOC concentrations reduce the ability of adsorption systems to remove VOC from an airstream. Low VOC concentration results in low partial pressure exerted. This partial pressure is the driving force for saturating the adsorption media to its full capacity. If the media cannot be saturated, a larger volume of adsorbent is required to hold the captured VOCs. Using a Carbon Adsorption Unit as an example, an increase in the volume of adsorbent will also increase:

- the number or size of tanks used to contain the carbon,
- the size of the blowers required to push the air through the carbon;
- the energy required to recharge the carbon;
- the amount of space required to house the system, and,

- the cost of the system.

At the low VOC concentrations expected to be generated by most shipyard processes, there may be insufficient “driving force” to keep VOCs adsorbed they may become naturally desorbed at a rate equal to or greater than the rate at which they are adsorbed. Thus, there will eventually be a level of VOCs in the airstream at which an adsorption control process will not perform. This effective concentration limit varies depending upon such factors as the specific VOCs in the process, the characteristics of the adsorbing media or the ambient climate such as temperature and humidity. Typical VOC concentrations at which the adsorption method is used and found to be effective ranges from 5,000 ppm down to 20 ppm.

The practicability of absorption in shipbuilding and repair VOC control processes is comparable to that of adsorption absorption processes also become less efficient as VOC concentrations decrease. The frequency at which VOCs will contact the absorbent decrease with a decrease in VOC concentration. To counter this phenomena a greater surface area of the absorbent must be exposed to the VOCs to increase the likelihood of absorption occurring. In the case of a packed tower type absorber, a larger tower or a greater number of towers is required to increase the surface area of the absorbing fluid. This size increase results in greater capital and operating costs of the system.

For condensation systems, low concentration is not necessarily a problem with removing VOCs from the air flow. Nevertheless, analogous to the problems discussed with incineration condensation processes must expend a great amount of energy to chill immense volumes of air. For a 27,000 CFM paint spray booth this is equivalent to chilling a 30 foot cube of air down to the condensation temperature of the VOCs every minute. In the case of the 200,000 CFM spray booth this cube would measure 58 feet on each side.

For good control efficiency, the concentration of VOCs within the air stream must be high. Due not only to the nature of the operations but also the size of the articles being coated, the concentration of VOCs within the air stream for most shipyard processes is very low. In reviewing the paint spray records of one shipyard it was determined that in painting a typical construction block the approximate volume of paint applied within one hour of spraying is slightly more than one gallon. If this painting was conducted in a 200,000 CFM spray booth as discussed previously and with a paint containing 3.5 pounds of VOC per gallon the concentration of VOCs in the airstream is calculated to be approximately 0.006 parts per million (ppm). In a smaller paint booth sized at 27,000 CFM, the airstream VOC concentration would be approximately 0.044 ppbn. If the rate of paint application was increased ten or a hundred-fold, the estimated airstream VOC concentration would still remain very low.

6.0 ALTERNATIVES TO CONTROL TECHNOLOGY

As advances are made in VOC emission control equipment technology, so are advances being made in coating performance technology. Over the last 15 years improvements have been made in coating formulations; improvements that resulted in a lower ratio of the volatile solvent portion to the solids portion in some coatings and greater durability. Coatings are continuously being re-formulated and tested. Some formulations are termed water-based and contain very little or no solvent concentration. The most difficult aspect of this re-formulation is the simultaneous reduction of the solvent content and preservation of the performance quality.

Coating application advances have increased the efficiency of transferring the coating material to the part to be coated. As transfer efficiency increases, the total volume of coating consumed in the coating process decreases; less coating is wasted collaterally. As a result, the VOCs emitted also decrease. Some coating application processes that are successful at reducing the overall amount of coating used in the Shipbuilding Industry are High Volume Low Pressure (HVLP) systems and airless spray equipment. Other systems, such as plural component systems that mix two-part paints at the spray gun, reduce the volume of coating used by reducing the amount of pre-mixed paint wasted.

One of the primary functions of organic solvents in a standard coating is to reduce the viscosity of the coating to a point where it can be readily atomized into a spray, carried to the surface of the part and deposited. Because the viscosity needed for proper atomization is less than the viscosity needed for film coalescence and surface leveling, most coatings are currently formulated so that much of the carrier solvent evaporates soon after deposition. In a recent study, supercritical fluids were investigated as a potential replacement for these viscosity reducing organic solvents.

SuperCritical fluids exist at temperatures and pressures near the critical point where the properties of liquid and gas are Similar; the fluid is simultaneously gas-like and liquid-like. Common liquids can become supercritical at high temperatures. The most widely used supercritical fluids are compressed gases such as carbon dioxide, ammonia nitrous oxide, ethane, ethylene and propane. These gases become supercritical at relatively moderate temperatures. SuperCritical fluids are highly soluble and have low viscosity when compared to organic solvents. Because they usually consist of very small molecules, they can also easily inter-penetrate the polymers and other solids of coatings.

Carbon dioxide is often used as a supercritical fluid because of its low cost and easy availability. Since carbon dioxide is a gas at ambient conditions, it is proportioned and mixed with the coating just prior to application. The coating as it is sprayed contains 10 to 50 percent by weight of carbon dioxide. To make the carbon dioxide supercritical, the spray solution is heated to a temperature of 40° to 70° Centigrade. This increase in temperature also offsets the cooling that occurs as the carbon dioxide expands into a gas as it is released from pressure when the solution is sprayed. As the coating sprays from the gun, atomization occurs not from the shearing forces encountered with the surrounding air but from the expansive forces of the supercritical fluid. The cooling of the coating material as it is sprayed suppresses the organic solvent evaporation until the coating reaches the surface, allowing proper film coalescence and surface leveling.

The use of supercritical fluids in spray applications is said to allow paint formulators to reduce VOC emissions up to 70 percent. Although it has only been demonstrated under test conditions, it is believed to be broadly applicable to most spray systems and easily retrofitted into existing spray operations. The technology has been demonstrated using acrylics, polyesters, cellulose, alkyds, and commercial paints and lacquers.

7.0 CONCLUSIONS

Shipyards operations exhibit wide diversity in the coatings used, a broad range in the size and shape of parts that require coating, and great variability in the volume of coatings applied on a day to day basis. Many factors must be considered when selecting Air Pollution Control Technologies. These include:

- the nature of the VOCs that must be controlled;
- the volume of air that must be handled
- the concentration of the VOCs within the airstream
- batch processes versus continuous operations;
- potential costs; and
- local state and federal laws and regulations.

Installation and operation of air pollution control equipment is expensive. In March 1987 the Aerospace Industry sponsored a State of the Industry Report regarding Aerospace surface coatings and solvents emission control. The report summarized estimated costs for Control Equipment if implemented at various aerospace facilities. Table 8.1 uses information from the aerospace report to show cost estimates developed for an assortment of system applications. Some of these estimates were generated using information from the EPA guideline series entitled Control of Volatile Organic Emissions from Existing Stationary Sources - Volume I: Control Methods for Surface Coating Operations, [EPA-450/2-76-028 (November 1976)]. The cost estimates presented in the table were developed in 1987 and should be adjusted to the present time accordingly. Because each installation presents unique conditions and problems, extrapolation of costs should be used for relative comparison only. The Aerospace estimates are provided to illustrate a basic range of expected Control Equipment expenditures.

TABLE 8.1

Control Equipment Cost Estimates
for Various Aerospace Coating Facilities*

<u>System Type</u>	<u>Flowrate (CFM)</u>	<u>Equipment Cost</u>	<u>Annual Operating Cost</u>
Carbon Adsorption	80,000	\$1,709,000	\$238,048
Carbon Adsorption	50,000	1,135,000	160,582
Carbon Adsorption	70,000	1,719,000	272,479
Carbon Adsorption	80,000	1,520,000	186,067
Carbon Adsorption	42,000	1,089,000	177,801
Carbon Adsorption	36,000	912,000	139,115
Incineration	120,000	3,000,000	786,067
Incineration	30,000	418,000	146,000
Incineration	15,000	330,000	103,000
Catalytic Inciner.	120,000	1,600,000	1,302,133
Catalytic Inciner.	30,000	633,000	187,000
Catalytic Inciner.	15,000	423,000	120,000

*Cost Estimates Developed in 1987

Pre-construction primer coating appears to be the shipyard coating operation that most readily lends itself to the application of control equipment technology. However, the volume of pre-construction priming at a shipyard is minor when compared to other coating operations. Capture and control of this air flow would likely result in a large capital investment in exchange for a small reduction of the total volume of VOCs released at a shipyard facility.

As environmental regulations become more restrictive, there is greater incentive to focus research on coating reformulation to improve coating performance and reduce solvent content. Reformulation avoids the technical problems associated with air pollution control equipment and provides a more thorough reduction in potential VOC emissions. In summary, the results of this report indicate that:

- Capture of the exhaust airstream from most shipyard coating operations is difficult;
- Volatile Organic Compound concentrations within the airstream of most shipyard spray booths would be extremely low and difficult to capture;
- Air Pollution Control Systems installed now may become obsolete in the near future as advances are made in coating technology;
- Breakdown of control equipment could lead to production shutdowns or regulatory compliance problems;
- Capital and operating costs for control equipment may be prohibitive to smaller shipyards; and
- Installation of control equipment systems would inhibit the further research and development of low VOC coatings.

APPENDIX

REFERENCES

- Ayer, J., and Darvin, C.H., "Split-Flow Exhaust Recirculation for the Economic Control of VOC Emissions from Paint Spray Booths", Presentation at the Air and Waste Management Association 83rd Annual Meeting and Exhibition June, 1990.
- Busby et al., "SuperCritical Fluid Spray Application Technology A Pollution Prevention Technology for the Future", Presentation at the Air and Waste Management Association 83rd Annual Meeting and Exhibition June, 1990.
- Darvin C.H., and Ayer, J., "Stratification of Particulate and VOC Pollutant in Paint Spray Booths", Presentation at the Air and Waste Management Association 83rd Annual Meeting and Exhibition June, 1990.
- "Guide to Solvent Waste Reduction Alternatives, Final Report", Prepared by ICF Consulting Associates, Incorporated for Toxic Substances Control Division California Department of Health Services, October, 1986.
- Holdren M., Rust S., Smith, R., and Koetz J. "Evaluation of .Cryogenic Trapping as a Means for Collecting Organic Compounds in Ambient Air", EPA-600/S4-85-002, Environmental Monitoring Systems Laboratory, Research Triangle Park North Carolina, 1985.
- Houghton F.R., and Wildman J., "Manufacture and Uses of Active Carbon", Chemical and Process Engineering, May, 1971.
- Kenson R.E., and Jackson J.F., "Catalytic Incineration of Emissions from a Carbon Adsorption/Air Recirculation System on a Paint Spray Booth", Presentation at the Air and Waste Management Association 82nd Annual Meeting & Exhibition June, 1989.
- Kosusko, M., and Nunez C., "Destruction of Volatile Organic Compounds Using Catalytic Oxidation", Air and Waste Management Association Vol. 40, No. 2, 1990.
- Kottke, L.R., "VOC Technology Catches Up To Regs", Environmental Protection Vol. 3, No. 2, 1992.
- Patkar, A., and Laznow, J., "Hazardous Air Pollutant Control Technologiess", Hazmat World, 'Vol. 5, No. 2, 1992.
- Ritts, D.H., "Evaluation of Innovative Volatile Organic Compound and Hazardous Air Pollutant Control Technologies for the U.S. Air Force Paint Spray Booths", Presentation at the Air and Waste Management Association 83rd Annual Meeting and Exhibition June, 1990.

“State of the Industry Report Aerospace Surface Coatings/Solvents, Equivalency/Alternate Emission Control”, Garrett Corporation General Dynamics, Hughes Aircraft Company, Lear Siegler, Lockheed-California Company, McDonnell Douglas Corporation Northrop Corporation Rockwell International Rohr Industries, The Boeing Company, TRW Incorporated 1987.

Wilcox J.B., and Agardy, F.J., “Thermal Destruction of Air Toxic VOC’s Using Packed Bed Technology”, Presentation at the Air and Waste Management Association 83rd Annual Meeting and Exhibition, June 1990.

ACRONYMS

BACM	Best Available Control Measures
BTU	British Thermal Unit
CAA	Clean Air Act
CFC	Chloroflourocarbon
CFM	Cubic Feet per Minute
CO	Carbon Monoxide
CPACI	Carbon Paper Adsorption catalytic Incineration
CTG	Control Technique Guideline
DRE	Destruction and Removal Efficiency
EPA	Environmental Protection Agency
FBCI	Fluidized-Bed Catalytic Incineration
HAPs	Hazardous Air Pollutants
LEL	Lower Explosion Limit
MACT	Maximum Achievable Control Technology
NIOSH	National Institute for Occupational Safety and Health
NSRP	National Shipbuilding Research Program
NO _x	Nitrogen Oxides
O ³	Ozone
OSHA	Occupational Safety and Health Administration
PPb	parts per billion
PPm	parts per million
TUHC	Total Unburned Hydrocarbons
USAF	United States Air Force
VOC	Volatile Organic Compound

